

Voltammetry of Chloroacetic Acids at the Solid Electrodes

Elene Kvaratskhelia¹ and Ramaz Kvaratskhelia¹

¹Georgian Academy of Sciences
Institute of Inorganic Chemistry and Electrochemistry
Mindely st.11
Tbilisi 380086
Republic of Georgia

Electrochemical behaviour of mono-, di- and trichloroacetic acids has been studied in the aqueous solutions at the electrodes from individual metals (Pt, Cu, Cd, Ta), amalgamated copper and alloys of Cd with Cu, Sn, Ni, In, Hg, Ag, Pb (investigation methods - voltammetry at the rotating disk electrodes and chronovoltammetry at the stationary electrodes). Monochloroacetic acid forms at all the used electrodes the waves of the hydrogen ions discharge process. Ill-defined first waves corresponding to the acid dechlorination process are also observed at the Cu and Cu-Hg electrodes. The well-defined wave of this process is observed only in case of the Cd-Cu (28-50% in 0.1M solution of sodium perchlorate is equal to -0.71V (s.c.e.). Voltammetry of dichloroacetic acid differs appreciably from voltammetry of monochloroacetic acid. At all the used electrodes dichloroacetic acid forms also the waves of the hydrogen ions discharge, but in case of the electrodes from Cu and alloys of Cd with Cu, Ni, In and Ag the waves of acid dechlorination are also observed. The half-wave potentials of these waves in 0.1M perchlorate solution are equal to -0.60V(Cu), -0.68–0.69V(Cd-Cu alloys), -0.73–0.74V(alloys of Cd with Ni, In, Ag). Particularly well-defined waves of the dichloroacetic acid dechlorination process are observed in case of the Cd-Cu alloys (28-50% exceed appreciably by height the waves observed at other electrodes. Changing of the composition of the Cd-Cu alloy does not exercise appreciable influence on the parameters of dechlorination wave. In case of the Cd-Ni (0.2-2% values of limiting current with a rise of the Ni content in the electrode increase appreciably. The lowest waves of dichloroacetic acid dechlorination process are formed at the electrodes from Cd-In and Cd-Ag alloys (up to 5% to the perchlorate solution causes a decrease of the dechlorination wave height. In the iodide solution (0.1M KI) the waves of the dechlorination of dichloroacetic acid are not observed: at the voltammograms only the waves of the hydrogen ions discharge are formed. Trichloroacetic acid shows the largest voltammetric activity. At all the used electrodes (excepting Pt and Ta) in the perchlorate solution the well-defined waves and chronovoltammetric peaks of the acid dechlorination process are observed (in case of Cu-Hg electrode wave is better pronounced in acidic solutions). Second waves at the voltammograms of trichloroacetic acid correspond to the hydrogen ions discharge process. The half-wave potential values of first waves of acid in perchlorate background are equal to -0.62V (Cu), -1.05V (Cu-Hg in 0.1M perchlorate solution with 0.005N sulfuric acid), -0.73–0.75V (Cd and alloys of Cd with Sn, Ni, In, Hg, Pb, Ag), -0.68–0.70V (Cd-Cu alloys with 15-70% trichloroacetic acid dechlorination process are observed in case of the electrodes from Cd-Cu

alloys with 28-50% acid). In case of the electrodes with higher or lower content of Cu the limiting current values are appreciably less. In case of the electrodes from Cd-Ni and Cd-Ag alloys an increase of the Ni and Ag content causes the rise of the dechlorination wave height. In case of the electrodes from Cd-Hg, Cd-In and Cd-Pb alloys an increase of the Hg, In and Pb content leads to the decrease of the first wave height. Changing of the Sn content in the Cd-Sn alloy from 0.2% limiting current values. Addition of the small amounts of sulfuric acid to the perchlorate solution causes an acceleration of the dechlorination process in case of the Cu-Hg electrode, but has not an appreciable influence on the limiting current values in case of other electrodes. In iodide background (0.1M KI) the waves of the dechlorination process are not observed (as in case of dichloroacetic acid).

The high values of the limiting current of first waves of di- and trichloroacetic acids in case of the electrodes from Cd-Cu alloys show that the full dechlorination of these acids takes place at these electrodes only. At other electrodes the partial dechlorination occurs. A pronounced influence of electrode nature on the rate of the dechlorination process and absence of the waves of this process in iodide background (which contains the well-adsorbable anions) testify to the fact that anions or molecules of di- and trichloroacetic acids adsorbed at the electrode from the direction of chlorine atoms undergo dechlorination. Because of the comparatively low adsorbability of chlorine atoms the competition between an adsorption of chloroacetic acids by chlorine atoms or by carboxyl group is possible. Therefore a participation of the anions of chloroacetic acids in the dechlorination process is more preferable because in this case an adsorption from the direction of carboxyl group is complicated by an existence of the negative charge. This fact causes an inhibition of the dechlorination of more weak dichloroacetic acid in acidic solutions and absence of any appreciable influence of the rise of the solution acidity on the dechlorination of more strong trichloroacetic acid. An acceleration of the dechlorination process in a series: monochloroacetic acid; dichloroacetic acid; trichloroacetic acid is connected, first of all, with a decrease of the C-Cl bond energy in this series (correspondingly 22.7 kJ/mole, 19.4 kJ/mole and 14.9 kJ/mole).